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Supplementary Information

Effects of solution chemistry on the attachment of graphene oxide onto clay minerals

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Calculation of DLVO interaction energy

According to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the total interaction energy between particle and collector (V_{TOT}) can be defined as the sum of two interactions, the attractive van der Waals interaction (V_{VDW}) and the repulsive electrostatic double layer interaction (V_{EDL}) [S1]:

$$V_{TOT} = V_{VDW} + V_{EDL} \tag{S1}$$

The van der Waals interaction is calculated using the Hamaker approach and Gregory's formulation [S2:]

$$V_{VDW} = -\frac{Ar_{NP}}{6h\left(1+\frac{14h}{\lambda}\right)} \tag{S2}$$

Where r_{NP} is the radius of GO nanoparticles, h is the separation distance between GO nanoparticles and quartz surface, λ is the characteristic wavelength of GO nanoparticle (λ = 100 nm), and A is the Hamaker constant. A =8.31×10^{-21} J [S3] was used for graphene particle- kaolinite interaction. For graphene- montmorillonite interaction, The Hamaker constant of GO nanoparticles-water- montmorillonite system can be calculated by following equation [S4]:

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{S5}$$

Where A_{132} is the Hamaker constant for the material 1 (GO nanoparticle) interaction with the material 2 (collector) through the material 3 (water), A_{11}, is the Hamaker constant of the GO, which is assumed to be 6.34×10^{-20}J, [S5] A_{22} is the Hamaker constant of the collector surface, which is 6.49×10^{-20} J, [S6] and A_{33} is the Hamaker constant of water, which is 3.70×10^{-20} J [S7]. Then, the Hamaker constant value of nanoparticles-water- montmorillonite system (A132) is obtained from above equations to be 3.70×10^{-21} J.

With the assumption of constant potential at the surface, the electrical double layer interaction can be calculated as [S8]:

$$V_{EDL} = \pi r_{NP} \varepsilon_0 \varepsilon_r \left\{ 2\phi_1\phi_2 \ln\left[\frac{1+\exp(-\kappa h)}{1-\exp(-\kappa h)}\right] + (\phi_1^{\ 2} + \phi_2^{\ 2}) \ln\left[1-\exp(-2\kappa h)\right] \right\} \qquad \text{(S3)}$$

where ε_0 is the vacuum permittivity (8.85×10^{-12} C^2/Jm), ε_r is the relative dielectric permittivity of water (78.4), ϕ_1 and ϕ_2 are the surface potentials of GO nanoparticles and clay, respectively, κ is the Debye reciprocal length and can be calculated as [S9]:

$$\kappa = \sqrt{\frac{2N_A e^2 I}{\varepsilon_r \varepsilon_0 K_B T}} \qquad \text{(S4)}$$

where N_A is the Avogadro number (6.02×10^{23} mol^{-1}), e is the electron charge (-1.60×10^{-19} C), I is the ionic strength of the background electrolyte, K_B is Boltzmann constant (1.38×10^{23} J/K), and T is Kelvin temperature (298 K).

Table S1. Selected Physicochemical Properties of Clay Minerals Tested

Clay minerals	Chemical composition	Total specific surface area (m^2/g)	pH_{PZC}[S10-S12]
Montmorillonite	$(OH)_4Si_8Al_4O_{20}$•nH_2O	49.4	2.5
Kaolinite	$Al_4[Si_4O_{10}](OH)_8$	19.8	3.8
Diatomite	SiO_2•nH_2O	1.6	1.5

Table S2. Comparison of the R^2 values of the two isotherm models tested in this work.

Type of clay	solution chemistry [a]	pH	R^2 of isotherm model	
			Freundlich	Langmuir
Diatomite	10 mM NaCl	5.0	0.981	0.809
Montmorillonite	1 mM NaCl	5.0	0.929	0.859
Montmorillonite	10 mM NaCl	5.0	0.988	0.924
Montmorillonite	20 mM NaCl	5.0	0.767	0.638
Kaolinite	1 mM NaCl	5.0	0.908	0.875
Kaolinite	10 mM NaCl	5.0	0.949	0.933
Kaolinite	20 mM NaCl	5.0	0.795	0.671
Montmorillonite	10 mM NaCl	7.0	0.991	0.989
Kaolinite	10 mM NaCl	7.0	0.857	0.806
Montmorillonite	10 mM NaCl	9.0	0.868	0.823
Kaolinite	10 mM NaCl	9.0	0.884	0.812
Montmorillonite	0.1 mM $CaCl_2$	5.0	0.887	0.786
Kaolinite	0.1 mM $CaCl_2$	5.0	0.817	0.658
Montmorillonite	0.3 mM $CaCl_2$	5.0	0.753	0.817
Kaolinite	0.3 mM $CaCl_2$	5.0	0.858	0.830
Montmorillonite	10 mM NaCl + 0.1 mM TA[a]	5.0	0.901	0.803
Kaolinite	10 mM NaCl + 0.1 mM TA	5.0	0.957	0.785

[a] TA represent tartaric acid.

Table S3. Calculated Maximum Energy Barriers (Φ_{max}) andThe Respective Separation Distances of Particle–Collector DLVO Interaction Energy Profiles

Type of clay	solution chemistry [a]	pH	ζ potential of GO[b] (mV)	$Z_{ave\text{-}GO}$[c] (nm)	ζ potential of clay [d] (mV)	Φ_{max}	
						height (K_BT)	distance (nm)
Diatomite	10 mM NaCl	5.0	-23.8 ± 0.4	256.3 ± 10.1	-25.2 ± 1.9	62.9	1.1
Montmorillonite	1 mM NaCl	5.0	-41.2 ± 1.1	192.8 ± 8.5	-15.8 ± 0.7	46.1	4.6
Montmorillonite	10 mM NaCl	5.0	-23.8 ± 0.4	256.3 ± 10.1	-11.6 ± 0.9	20.6	1.8
Montmorillonite	20 mM NaCl	5.0	-18.7 ± 0.9	283.2 ± 13.7	-8.6 ± 0.9	5.79	2.0
Kaolinite	1 mM NaCl	5.0	-41.2 ± 1.1	192.8 ± 8.5	-16.9 ± 0.5	65.6	4.4
Kaolinite	10 mM NaCl	5.0	-23.8 ± 0.4	256.3 ± 10.1	-12.2 ± 0.2	13.8	2.5
Kaolinite	20 mM NaCl	5.0	-18.7 ± 0.9	283.2 ± 13.7	-10.3 ± 0.2	1.1	2.5
Montmorillonite	10 mM NaCl	7.0	-26.4 ± 0.5	245.1 ± 9.2	-14.8 ± 0.4	34.2	1.4
Kaolinite	10 mM NaCl	7.0	-26.4 ± 0.5	245.1 ± 9.2	-25.7 ± 0.7	61.6	1.3
Montmorillonite	10 mM NaCl	9.0	-29.6 ± 0.3	228.8 ± 4.5	-21.8 ± 1.2	66.6	1.0
Kaolinite	10 mM NaCl	9.0	-29.6 ± 0.3	228.8 ± 4.5	-33.6 ± 0.6	102.9	1.1
Montmorillonite	0.1 mM $CaCl_2$	5.0	-23.2 ± 1.2	232.5 ± 6.9	-25.5 ± 0.8	89.4	2.7
Kaolinite	0.1 mM $CaCl_2$	5.0	-23.2 ± 1.2	232.5 ± 6.9	-25.6 ± 1.7	81.8	2.3
Montmorillonite	0.3 mM $CaCl_2$	5.0	-20.6 ± 0.4	276.6 ± 12.3	-23.6 ± 0.9	78.6	4.0
Kaolinite	0.3 mM $CaCl_2$	5.0	-20.6 ± 0.4	276.6 ± 12.3	-24.8 ± 1.1	78.9	3.8
Montmorillonite	10 mM NaCl + 0.1 mM TA[a]	5.0	-22.1 ± 0.7	175.5 ± 7.3	-21.3 ± 0.2	57.1	1.1
Kaolinite	10 mM NaCl + 0.1 mM TA	5.0	-22.1 ± 0.7	175.5 ± 7.3	-20.5 ± 0.6	70.2	3.5

[a] TA represent tartaric acid.

[b] Zeta potential of GO; values after ± sign represent standard deviation of three replicates.

[c] Hydrodynamic diameter of GO based on DLS analysis, values after ± sign represent standard deviation of three replicates.

[d] Zeta potential of clay mineral; values after ± sign represent standard deviation of three replicates.

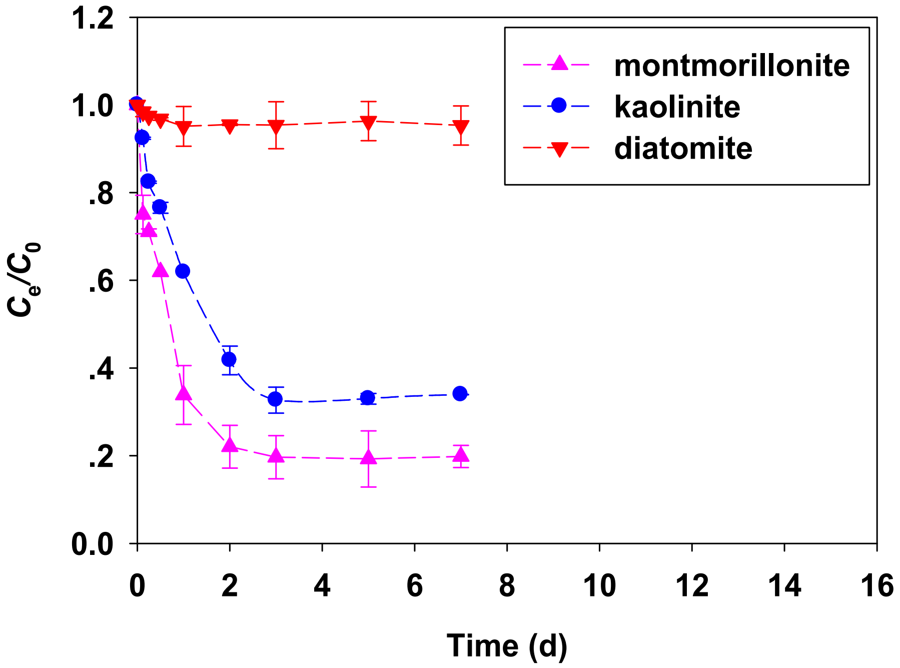

Fig. S1 Time required to reach equilibrium attachment of GO to clay (m_{clay}=0.1 g). C_e is the concentration of GO in liquid phase at time t; C_0 (15 mg/L) is the total GO concentration in the solution at t = 0. Error bars indicate standard deviation of triplicate samples.

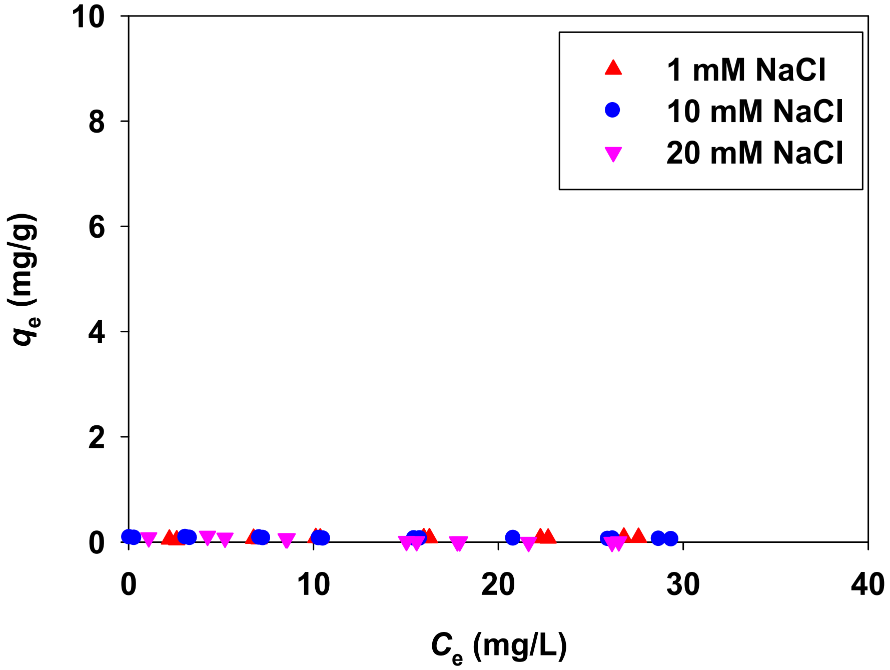

Fig. S2 Effect of ionic strength on the attachment of GO onto diatomite.

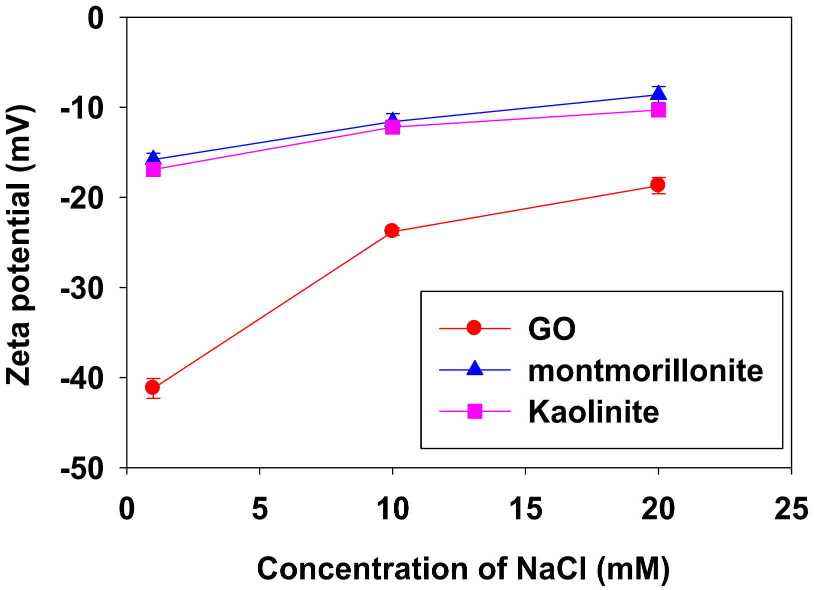

Fig. S3 Zeta potential of GO and clay minerals in three different concentrations of NaCl solution. Error bars indicate standard deviation of triplicate samples.

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